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# Acrylamide Homopolymers and Acrylamide–*N*-Isopropylacrylamide Block Copolymers by Atomic Transfer Radical Polymerization in Water

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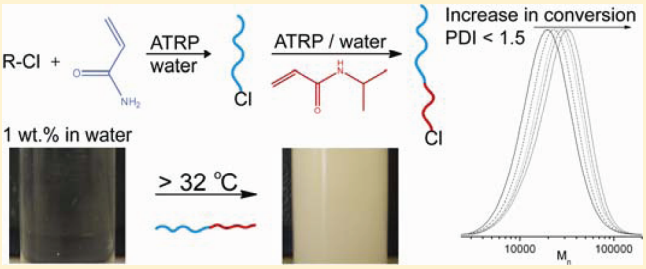
**ABSTRACT:** Atomic transfer radical polymerization (ATRP) of acrylamide has been accomplished in aqueous media at room temperature. By using methyl 2-chloropropionate (MeClPr) as the initiator and tris[2-(dimethylamino)ethyl]-amine ($Me_6$TREN)/copper halogenide (CuX) as the catalyst system, different linear polyacrylamides with apparent molecular weights up to >150 000 g/mol were synthesized with dispersities as low as 1.39. The molecular weights agreed well with the theoretical ones at relatively low-medium monomer/initiator ratios (<700:1). Initial chain extension experiments (isolated macroinitiator) resulted in a polymer with bimodal distribution. However, *in situ* chain extension experiments, carried out by addition of a second fresh batch of monomer to the reaction mixture, confirmed the living nature of the polymerization. By adding a fresh batch of monomer to a linear macroinitiator ($M_n$ = 22 780 g/mol, PDI = 1.42) in solution, an increase in the molecular weight up to 30 220 g/mol (PDI = 1.64) was observed. In addition, linear polyacrylamides were used as macroinitiators for the synthesis of block copolymers polyacrylamide-*b*-poly(*N*-isopropylacrylamide).




## INTRODUCTION

Polyacrylamide (PAM) and its derivatives are widely used in cosmetics, biomedical applications, wastewater treatment, and oil recovery.[1,2] Although their synthesis has been extensively studied, the focus now lies mainly on the control of the polymerization process through living radical polymerization strategies.[3−9] Atomic transfer radical polymerization (ATRP), a living radical polymerization technique, allows the synthesis of polymers with well-defined molecular weights and dispersities (PDI < 1.5).[10,11] This technique is widely used for monomers such as (functionalized) styrenes,[12] (meth)acrylates,[12] and acrylonitrile,[13] but its use to polymerize acrylamide and its derivatives is limited.

Generally speaking, the ATRP of water-soluble monomers still represents a challenge with respect to the control of the polymerization when using water as the only solvent.[14] ATRP of acrylamide (and its derivatives) has in general been tried in organic solvents (methanol,[15] ethanol,[16] toluene,[3,16] dimethylformamide[16] [DMF], 2-propanol[17]) and mixtures of organic solvents with water (ethanol–water[18,19] [4−1 and 7−3, v/v], DMF–water[20] [range between 1−1 to 7−3, v/v], and glycerol–water[4,5,11,21] [1−1, v/v]). The negative aspects of water on ATRP can be mitigated by performing the polymerizations in an organic–water mixture at low (0 °C) temperatures.[22] ATRP of acrylamide in water at elevated temperatures (>80 °C) has also been reported.[4,11,23] Low dispersity PAM could be prepared using an activator generated by electron transfer ATRP in water at room temperature.[24] However, the apparent molecular weights were relatively low (<6000 g/mol).

Regarding ATRP in water solution, good results in terms of dispersity and predictability of molecular weight have been published for few systems.[25,26] However, several investigations on the ATRP of hydrophilic acrylic monomers conducted in aqueous solutions showed that the process is difficult to control, unless the polymerization rate is slowed down by adding a cosolvent (usually an alcohol) or a Cu(II) salt.[14,27−29]

Successful ATRP has been accomplished for several derivatives of acrylamide,[3,15,16,18] such as *N*-hydroxyethylacrylamide, *N*,*N*-dimethylacrylamide, *N*-*tert*-butylacrylamide, and *N*-(2-hydroxypropyl)methacrylamide. However, the focus was not on acrylamide itself. To the best of our knowledge, only few publications[4,5,11,23] mentioned the controlled polymerization of acrylamide using chloroacetic acid, 2-chloropropionamide (2-Cl-PA), or 2-bromopropionamide (2-Br-PA) as initiators and either CuCl/*N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA) or 2,2-bipyridine (bpy) as catalytic systems. Although the molecular weight of the polyacrylamide increases linearly with conversion,[5,23] the apparent (determined by gel permeation chromatography, GPC) molecular weight differed significantly from the theoretical one.

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Table 1. Homopolymerization of Acrylamide under Different Conditions

| entry | $[M]_0$:$[I]_0$:$[CuCl]_0$:$[Me_6TREN]_0$[a] | M/water (w:v), $T$ (°C), time (min) | conv (%) | $M_{n,th}$ | $M_{n,GPC}$ | PDI |
|---|---|---|---|---|---|---|
| 1 | 225:1:2:2 | 1:4; 25; 60 | 48.7 | 7 719 | 10 230 | |
| 2 | 385:1:6.0:6.0 | 1:6; 25; 60 | 28.2 | 7 717 | 11 900 | 1.40 |
| 3 | 385:1:1.5:1.5 | 1:4; 25; 60 | 88.2 | 24 011 | 22 780 | 1.42 |
| 4 | 470:1:1.5:1.5 | 1:6; 25; 30 | 69.8 | 23 269 | 22 863 | 1.42 |
| 5 | 500:1:1.5:1.5 | 1:12; 25; 60 | 42.2 | 14 998 | 16 780 | 1.88 |
| 6 | 680:1:1.5:1.5 | 1:6; 25; 90 | 78.3 | 37 901 | 32 680 | 1.56 |
| 7 | 870:1:1.5:1.5 | 1:6; 25; 2 | 47.3 | 29 284 | 26 260 | 1.46 |
| 8 | 945:1:1.5:1.5 | 1:6; 25; 3 | 36.8 | 24 719 | 25 850 | 1.54 |
| 9 | 965:1:1.5:1.5 | 1:6; 25; 60 | 75.3 | 51 703 | 38 310 | 1.57 |
| 10[b] | 1000:1:1.5:1.5 | 1:15; 25; 60 | 52.0 | 28 762 | 41 970 | 1.97 |
| 11 | 1625:1:1.5:1.5 | 1:6; 25; 60 | 84.7 | 97 833 | 68 370 | 2.04 |
| 12 | 2785:1:1.5[c]:1.5 | 1:6; 25; 60 | 58.5 | 115 805 | 75 880 | 2.05 |
| 13 | 4355:1:1.5:1.5 | 1:6; 25; 60 | 69.1 | 213 852 | 108 800 | 2.30 |

[a]Molar ratio. [b]No increase in molecular weight with increase in conversion. [c]CuBr was used.

The ATRP of acrylamide was investigated in more detail using bpy, pentamethyldiethylenetriamine (PMDETA), hexamethyltriethylenetetraamine (HMTETA), TMEDA, or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ($Me_4$Cyclam) as ligands.[4] Although the average molecular weight increased with conversion, no concordance between the theoretical and experimental values was achieved. Only with the extraneous addition of copper(II) did the theoretical molecular weight (conversion·$\{[M]_0:[I]_0\}$) agree well with the actual one (apparent $M_n$ as measured by GPC), where the role of copper(II) consists in ensuring a fast deactivation rate in order to achieve relatively low dispersity values.[30] Nevertheless, the dispersities of the subsequent polymers were relatively high (PDI ≥ 1.6), indicating a difficult control of the polymerization. By using PMDETA and a lower temperature (90 °C instead of 130 °C), a reduction of the dispersity to 1.24 was achieved;[11] however, when higher molecular weight (>5000 g/mol) polymers were synthesized, using the chloride system, the dispersity increased significantly (PDI > 1.6).[11] A low dispersity linear PAM, whose molecular weight matched the theoretical one, could be synthesized using the bromide system (and addition of extraneous Cu(II)Br).[11]

ATRP of acrylamide has also been claimed in aqueous media;[24] however, the molecular weight again did not match the theoretical one. Terminated polyacrylamide (loss of the halogen group) has been reported following the ATRP of AM using 2-Cl-PA/CuCl/$Me_6$TREN as the initiator/catalyst system in a DMF−water (50−70 vol % DMF) solution.[20] Chain extension experiments failed due to the loss of the halogen group.[20]

Successful surface initiated ATRP of acrylamide has also been claimed in DMF using bpy-based copper complexes.[31−34] However, it has been concluded that bpy-based copper complexes fail to initiate the polymerization of acrylamide.[15,16,35] In addition, deactivation of the catalyst, through complexation by acrylamide or polyacrylamide, limits the conversion.

As evident from the above discussion, the ATRP of acrylamide still constitutes a significant hurdle in the science of living radical polymerization. ATRP of acrylamide has been accomplished in aqueous media using MeClPr/$Me_6$TREN/CuCl as the initiation/catalyst system. The molecular weight of the polymers increased linearly with conversion, and the dispersity remained relatively low. Chain extension experiments confirmed the living nature of the polymerizations in aqueous media. In addition, well-defined polyacrylamide-*b*-poly(*N*-isopropylacrylamide) block copolymers were synthesized.

## EXPERIMENTAL SECTION

**Chemicals.** Acrylamide (AM, electrophoresis grade, ≥99%), *N*-isopropylacrylamide (NIPAM, 97%), tris[2-(dimethylamino)ethyl]-amine ($Me_6$TREN), copper(I) bromide (CuBr, 98%), copper(I) chloride (CuCl, 98%), glacial acetic acid, ethanol, diethyl ether, and methyl 2-chloropropionate (MeClPr, 97%) were purchased from Sigma-Aldrich. CuBr and CuCl were purified by stirring in glacial acetic acid for at least 5 h, filtering, and washing with glacial acetic acid, ethanol, and diethyl ether (in that order) and then dried at reduced pressure. All the other chemicals were reagent grade and used without further purification.

**ATRP of AM in Aqueous Media.** A 250 mL three-necked flask was charged with the solid chemical (AM). A magnetic stirrer and distilled water were added and subsequently degassed by three freeze−pump−thaw cycles and left under nitrogen. The flask was then placed in an oil bath at 25 °C. Afterward CuCl and $Me_6$TREN were added, and the mixture was stirred for 10 min. The reaction was started by adding the initiator using a syringe. All the operations were carried out under nitrogen. After the reaction the mixture was exposed to air and the polymer was precipitated in a 10-fold amount of methanol. The polymer was dried in an oven at 65 °C up to constant weight. Detailed reaction conditions are summarized in Table 1.

**Kinetic Experiments.** Aliquots of the reaction mixture were removed at different time intervals using a degassed syringe. The aliquots were immediately frozen in liquid nitrogen. A portion was used for conversion measurements with GC, and the remaining part was diluted with distilled water and analyzed with GPC (after precipitation).

**Chain Extension Experiments.** Two different methods of chain extension were carried out: two-step or single-step *in situ* chain extension. For the two-step method, acrylamide was polymerized using the ATRP method as described earlier. The polymer was isolated, after a 1 h reaction, by precipitation in methanol and characterized. A 100 mL three-necked flask was charged with the solid chemicals (macroinitiator (PAM), & AM). A magnetic stirrer and distilled water were added, and subsequently the mixture was degassed by three freeze−pump−thaw cycles, after which CuBr was added. The flask was placed in an oil bath at 25 °C, and the reaction was started by the addition of $Me_6$TREN under nitrogen. The polymerization was continued for 22 h. The polymer was then isolated and characterized.

For the *in situ* method, acrylamide was polymerized using the ATRP method as described before. After 1 h of reaction an aliquot was taken for analysis. After this, a fresh batch of AM/$Me_6$TREN/CuBr was added under nitrogen. The polymerization with the fresh batch was continued for a further period of 2 h, after which a sample was taken for analysis.


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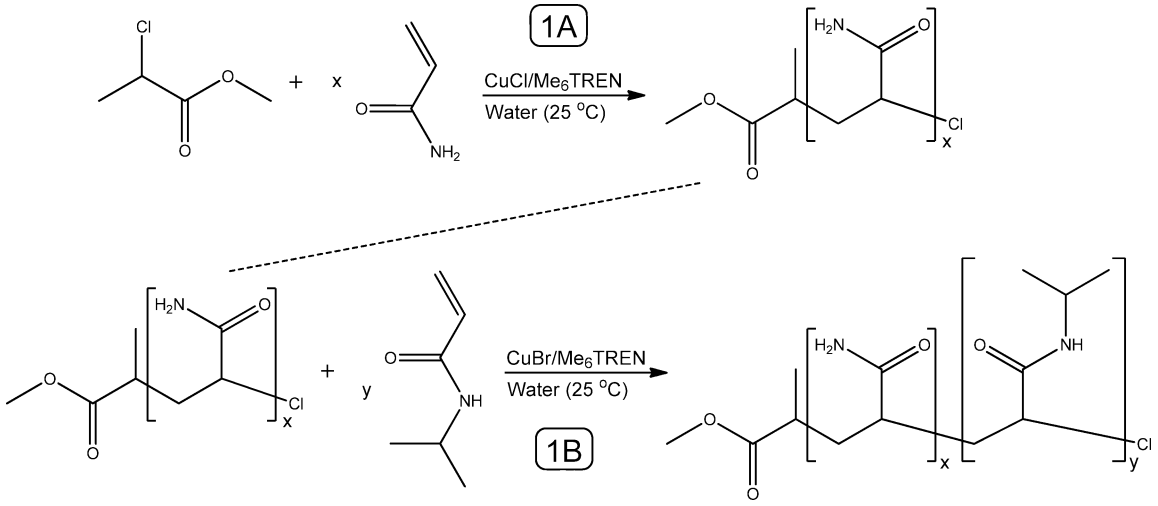
**Scheme 1. (A) Homopolymerization of AM and (B) Block Copolymerization of AM and NIPAM**




**Block Copolymerization, Synthesis of PAM-*b*-PNIPAM.** The macroinitiator PAM-Cl was synthesized according to the aforementioned procedure. To a round-bottomed flask 0.42 g (0.0178 mmol) of the macroinitiator was added along with NIPAM (1 g, 8.4 mmol). Double distilled water was added, and the mixture was degassed by three freeze–pump–thaw cycles followed by the addition of the catalyst. The flask was placed in a thermostated oil bath at 25 °C. To start the reaction, the ligand was added. All operations were carried out under nitrogen.

A sample of the synthesized block copolymer PAM-*b*-PNIPAM was thoroughly washed five times with THF. The washed sample was dried in an oven at 65 °C. A $^1$H NMR spectrum was recorded for both the washed and virgin samples.

**Characterization.** The acrylamide conversion was measured using gas chromatography (GC). The samples were dissolved in acetone (polymer precipitates), filtered or decanted, and injected on a Hewlett-Packard 5890 GC with an Elite-Wax ETR column.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. For analysis $D_2O$ was used as the solvent.

Gel permeation chromatography (GPC) analysis of all the water-soluble samples was performed on a Agilent 1200 system with Polymer Standard Service (PSS) columns (guard, $10^4$ and $10^3$ Å) with a 50 mM $NaNO_3$ aqueous solution as the eluent. The columns were operated at 40 °C with a flow rate of 1.00 mL/min, and a refractive index (RI) detector (Agilent 1200) was used at 40 °C. The apparent molecular weights and dispersities were determined using a polyacrylamide (PAM)-based calibration with WinGPC software (PSS).

## RESULTS AND DISCUSSION

**ATPR of Acrylamide.** The homopolymerization and block copolymerization (with NIPAM) experiments of acrylamide were performed according to Scheme 1.

The parameters that varied were the amount of solvent and the monomer/initiator/catalyst ratios (Table 1). As can be observed, PAM of relatively high molecular weights, up to 40 000 g/mol, can be prepared with relatively low dispersities.

The kinetic plot of the disappearance of AM is nonlinear (Figure 1), which is in line with earlier publications on the ATRP of AM[4,11] and derivatives thereof.[3,4,11,15,16] The kinetics of living radical polymerization can be divided into the stationary (quasi-equilibrium) state and a state exhibiting a power law dependence in time of the conversion index ($\ln[M_0/M]$),[36] a function of the monomer concentration at any given time $t$ (M), and at time zero ($M_0$). In the stationary state the conversion index ($\ln[M_0/M]$) is represented by eq 1.

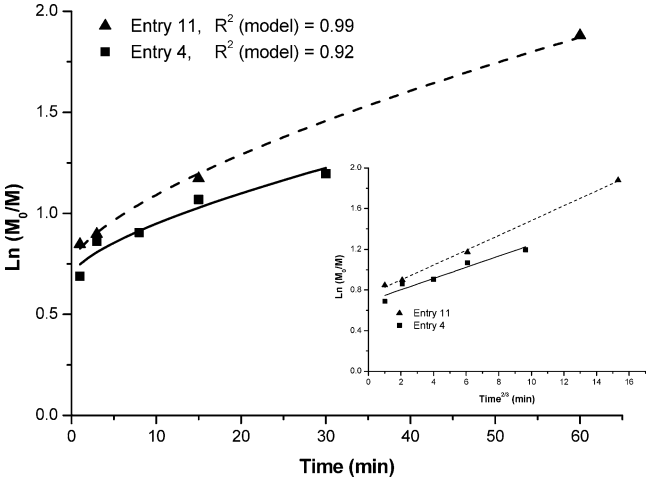



**Figure 1.** Kinetic plot for the ATRP of AM (entries 4 and 11, Table 1), big plot on a linear time scale, and inset on a scale of time$^{2/3}$.

$$\ln\left(\frac{[M]_0}{M}\right) = k_p\left(\frac{R_i}{k_t}\right)^{1/2} t \quad (1)$$

where $k_p$ indicates the kinetic constant for propagation, $R_i$ the initiation rate, and $k_t$ the termination rate constant.

In the case where initiation does not follow the conventional system and the starting concentration of radicals equals zero ($[X^*]_0 = 0$, $[X^*]_0$ equals the radical concentration at time zero), the conversion index ($\ln[M_0/M]$) is represented by eq 2.[36]

$$\ln\left(\frac{[M]_0}{M}\right) = \frac{3}{2}k_p\left(\frac{K_{AT}[A]I_0}{3k_t}\right)^{1/3} t^{2/3} \quad (2)$$

where $K_{AT}$ is the equilibrium constant in ATRP ($K_{AT} = k_a/k_{da}$, $k_a$ is the activation rate constant and $k_{da}$ is the deactivation rate constant in ATRP).

In most ATRP systems the kinetics of the reaction crosses over from the power law dependence to the quasi-equilibrium within 1 min after starting the reaction. Using eq 2, we model the kinetics of the ATRP of AM (Figure 1).

A straight line should be obtained when the time scale is adjusted to the exponent (2/3).[36] Indeed, a good correlation is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obtained (inset, Figure 1) on a time scale of $t^{2/3}$. Although the nonlinearity of the kinetic plot is an indication of the presence of termination reactions,[16] given the results of the chain extension experiments, the nonlinearity arises due to a progressive deactivation of the catalyst by complexation with the growing polyacrylamide chains.[15,16] Moreover, the molecular weights increased linearly with conversion and the $M_n$ values were in good agreement (especially at medium molecular weights) with the theoretical values (Figure 2).

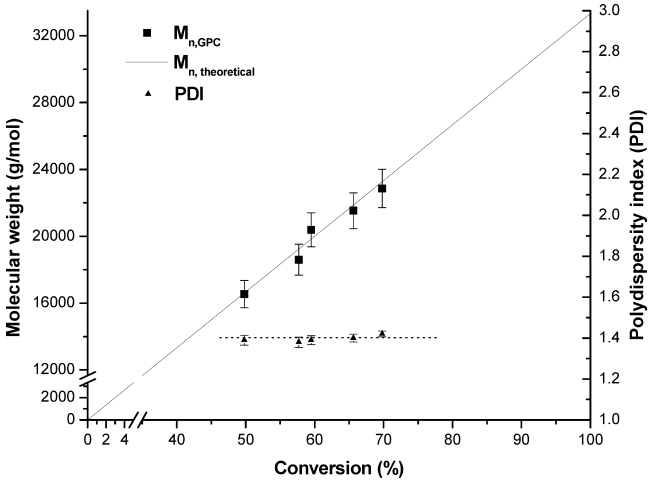


**Figure 2.** Dependence of the $M_n$ and PDI on the conversion of AM (entry 4, Table 1); dotted line serves as a guide.

Low molecular weight tailing has been observed in the GPC traces when attempting to demonstrate the ATRP of DMAA in toluene using the same CuCl/$Me_6$TREN/MeClPr initiator/catalyst system.[3] The only difference with the present system (despite the monomer) is the lower monomer/solvent ratio.[3] However, in the present case (Figure 3), the low molecular weight tailing in the GPC traces of the ATRP of acrylamide is not as pronounced as with the ATRP of DMAA.

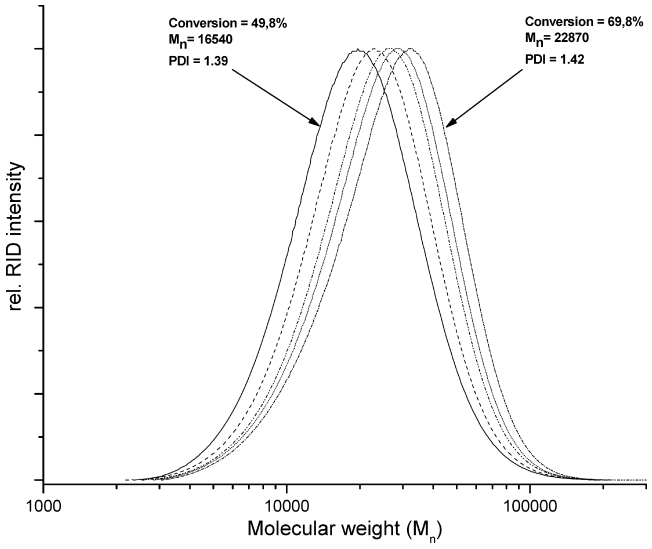


**Figure 3.** GPC traces of the PAM (entry 4, Table 1), conditions $[AM]_0$:$[MeClPr]_0$:$[CuCl]_0$:$[Me_6TREN]_0$ = 470:1:1.5:1.5; AM:solvent = 1:6 (w/v); solvent = water, $T$ = 25 °C.

On the other hand, a significant deviation of the molecular weight from the theoretical one is observed at conversions higher than 70% (Table 1), which is more pronounced when using high monomer to initiator ratios (entries 6–11) or higher amounts of catalyst/ligand (entries 1 and 2). When the amount of solvent was increased (entries 5 and 10), the control of the polymerization was lost, as also reported for the ATRP of NIPAM in isopropanol.[17] Although the molecular weight of the polymer is similar to the one prepared with a lower amount of solvent (entries 4 and 9), the PDI is significantly higher, the conversion is limited (similar to other results for DMAA in toluene[3]), and no increase in molecular weight with increase in conversion was observed (data not shown for brevity).

The dispersities of the PAM (entries 1–9, except entry 5) are lower compared to the ATRP of acrylamide in water and/or water–glycerol mixture at elevated temperatures,[4] which to this point are the best results on ATRP of AM in water. In an attempt to prepare higher molecular weight PAM (entries 11–13 in Table 1), higher monomer to initiator ratios were used. Although higher molecular weight PAM could be prepared, the dispersities of the polymers are relatively high. In spite of this, the linear increase of the molecular weight with conversion indicates a controlled radical polymerization[37] (except entries 5 and 10). In addition, similarly to entry 4 (Table 1), the extent of low molecular weight tailing is not significant (Figure 4).

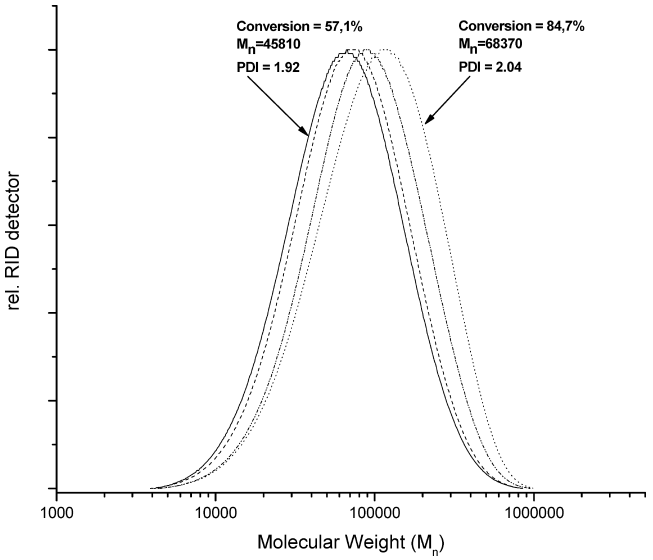


**Figure 4.** GPC traces of the PAM (entry 11, Table 1), conditions $[AM]_0$:$[MeClPr]_0$:$[CuCl]_0$:$[Me_6TREN]_0$ = 1625:1:1.5:1.5; AM:solvent = 1:6 (w/v); solvent = water, $T$ = 25 °C.

Given the high reaction rate of the catalyst system, the viscosity of the reaction medium quickly increases (when using high monomer/initiator ratios), and this might lead to mass transfer limitations.

As commonly accepted, for a successful ATRP, several conditions should be met. These conditions are[30,38] low dispersities (1.0 < PDI < 1.5) throughout the reaction, linear increase of the molecular weight with conversion, and good concordance between the theoretical molecular weights with the experimental values (and chain extensions[4]). The present system, MeClPr/CuCl/$Me_6$TREN in water, meets all these parameters, which is in stark contrast to the ATRP of AM in DMF–water mixture.[20] It can be speculated that the use of


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DMF−water in conjunction with a halide salt (LiCl, KCl, or $NH_4Cl$) enhances the rate of termination leading to a dead polymer.[20]

**Chain Extension Experiment, Two-Step.** As mentioned in the Experimental Section, two different approaches were tried in extending the PAM chains. Figure 5 displays the GPC

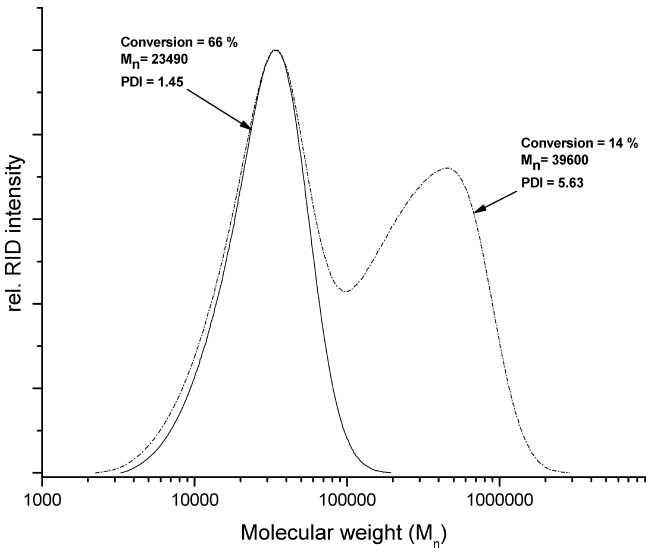


**Figure 5.** GPC traces for the two-step chain extension experiment.

results of the two-step approach. First the macroinitiator was prepared by the ATRP of AM. After a 1 h reaction period, a conversion of 66% (gravimetrically) was reached, yielding the PAM-Cl macroinitiator ($M_n$ = 23 490 g/mol, PDI = 1.45). In the second stage, the same concentration of AM was used. After a 22 h reaction period a conversion of 14% (gravimetrically determined) was reached. The GPC trace of the chain extended macroinitiator is bimodal (Figure 5) with an $M_n$ = 39 600 g/mol and a PDI of 5.63. This result clearly indicates that a portion of the chains cannot be initiated, even with the principle of halogen exchange.[39,40] This result is similar to the chain extensions of either a polystyrene or poly(*n*-butyl acrylate) with methyl methacrylate.[41] The poor initiation efficiency of the macroinitiator leads to the bimodal distribution (Figure 5). The halogen groups on the macroinitiator are primary halogens, which are known to have much lower activation rates compared to their secondary or tertiary analogues.[42,43] This fact explains the difficulty in activating the PAM macroinitiator. Nevertheless, the bimodal GPC trace indicates the presence of the halogen group on the macroinitiator. Initial results on the chain extensions of polystyrene and poly(*n*-butyl acrylate) with methyl methacrylate (MMA) displayed bimodal GPC traces.[41] The bimodal GPC traces were attributed to poor initiation efficiency, and the problem was mitigated by using 10 mol % of styrene in the monomer.[41] This is in stark contrast to the ATRP of AM (loss of halogen group, i.e., dead polymer) in a water/DMF solution (1:1) using 2-Cl-PA/$Me_6$TREN/CuCl as the initiator/catalyst system.[20]

**Chain Extension Experiment, *in Situ*.** Figure 6 shows the GPC results of the *in situ* chain extension approach.

As mentioned earlier, the difference here is that the macroinitiator is not isolated (by precipitation in methanol). After a 1 h reaction period, a conversion of 88.2% was reached, yielding the PAM-Cl macroinitiator ($M_n$ = 22 780 g/mol [$M_{n,th}$ = 24 011 g/mol], PDI = 1.42). After this, a second batch containing the same concentration of monomer, catalyst (halogen exchange principle), and ligand was added. The conversion of AM (second block) reached 25.5% after 2 h. The chain extended polymer had a $M_n$ of 30 220 g/mol and a PDI of 1.64 ($M_{n,th}$ = 30 953). This result reinforces the aforementioned conclusion that the halogen group is not lost during the ATRP of AM.

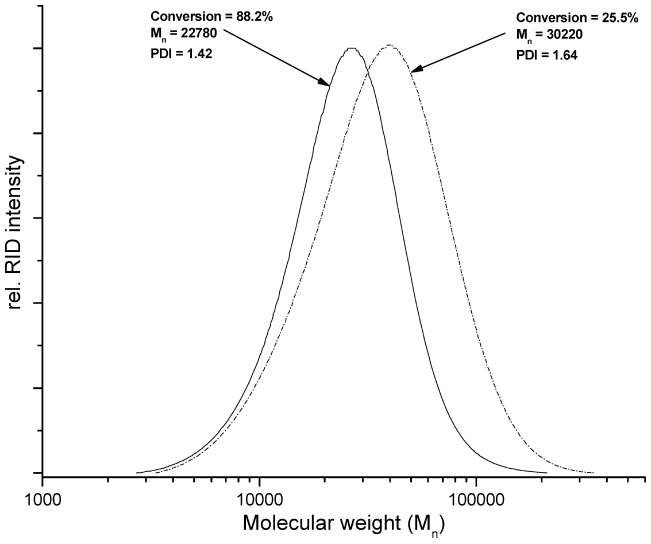


**Figure 6.** GPC traces for the *in situ* chain extension experiment.

**Block Copolymerization, Synthesis of PAM-*b*-PNIPAM.** As it is known that thermoresponsive[44] polymers offer control over viscosity by temperature variation, the above-mentioned polymer has been functionalized with NIPAM-based blocks. Several PAM-*b*-PNIPAM block copolymers were prepared according to Scheme 1B. These block copolymers have a low dispersity (PDI = 1.48) and a monomodal distribution. For brevity, Figure 7 displays only the $^1$H NMR spectra of one example of a PAM-*b*-PNIPAM block copolymer and of the THF washed equivalent.

The conversion of NIPAM was determined by using the ratio between the NMR resonances of AM and NIPAM units. The conversion equaled 5% corresponding to a degree of polymer-

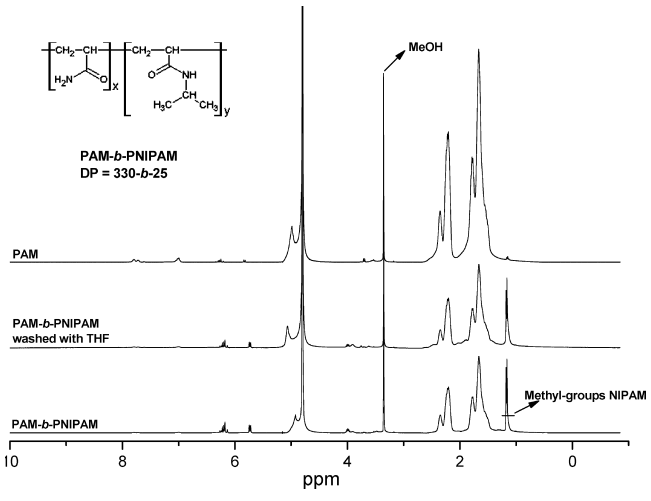


**Figure 7.** NMR spectra of PAM-*b*-PNIPAM (virgin and THF washed) and PAM.


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ization (DP) of 25 and a $M_n$ of 2811 g/mol. In addition, washing with THF did not change the ratio between the resonances of the AM and NIPAM units. This confirms that the NIPAM units are covalently linked to the PAM macroinitiator.

## ■ CONCLUSION

ATRP of acrylamide has been accomplished in water using the MeClPr/$Me_6$TREN/CuCl as the initiator/catalyst system. The molecular weights were in good agreement with the theoretical values. Linear PAM with apparent molecular weights up to >150 000 g/mol and dispersities as low as 1.39 could be prepared. Although the dispersities are higher than for ATRP of styrene and acrylates, both (two-step and *in situ*) chain extension experiments proved the living nature of the polymerizations. In addition, the well-defined block copolymer (PAM-*b*-PNIPAM, DP 330-*b*-25) was synthesized using the linear macroinitiator (PAM-Cl) prepared by the ATRP of AM in water. The possibility to synthesize well-defined linear homo- and block copolymers in water solution and under mild conditions can be highly attractive for industrial applications.

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### Notes

The authors declare no competing financial interest.

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